

**Combined NO<sub>x</sub>/SO<sub>2</sub> Removal from Flue Gas  
Using Ferrous Chelates of SH-Containing Amino Acids and Alkali**

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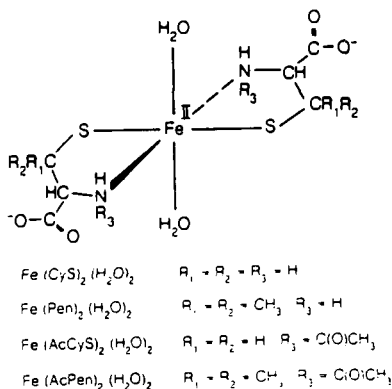
**ABSTRACT**

We report herein the use of ferrous chelates of SH-containing amino acids including cysteine, penicillamine, N-acetylcysteine, and N-acetylpencillamine in neutral or alkaline solutions for the combined removal of NO and SO<sub>2</sub> in wet flue gas clean-up systems. These SH-containing amino acids not only can stabilize ferrous ions in alkaline solutions to promote the absorption of NO, but are also capable of rapidly reducing ferric ions formed during the scrubbing process back to ferrous ions. The disulfide from of the above amino acids can be reduced by SO<sub>2</sub> and H<sub>2</sub>S to regenerate the starting monomeric species. The chemistry relevant to the absorption of NO by the above ferrous chelates and the ligand regeneration process will be discussed.

## INTRODUCTION

A large number of wet flue gas clean-up processes using iron chelates to simultaneously remove  $\text{NO}_x$  and  $\text{SO}_2$  from combustion flue gas have been developed over the past fifteen years. The mechanism for NO absorption using these  $\text{Fe}^{2+}$ (EDTA) type chelates involves the formation and subsequent reaction of a ferrous nitrosyl complex with dissolved  $\text{SO}_2$  and  $\text{O}_2$  to produce  $\text{N}_2$ ,  $\text{N}_2\text{O}$ , dithionate, sulfate, nitrogen-sulfur compounds, and ferric chelates which are unreactive towards NO (1). The regeneration of scrubbing liquors and ferrous chelates associated with such processes is very costly (2). Therefore, these wet absorption processes, even though very efficient in  $\text{SO}_2$  and  $\text{NO}_x$  removal, have not yet reached the commercial stage.

We wish to report the use of ferrous chelates of SH-containing amino acids (or thioamino acids) in neutral or alkaline solutions for the simultaneous removal of  $\text{NO}_x$  and  $\text{SO}_2$  from flue gas. The ferrous chelates investigated in this study include those of L-cysteine (CySH), DL-penicillamine (Pen), N-acetyl-L-cysteine (AcCySH), and N-acetyl-DL-penicillamine (AcPen).



The stereoisomers or racemates of the thioamino acids employed represent the most common and therefore least expensive forms; other stereoisomers or racemates can also be used since they should have identical chemical reactivities. Recent reports from our laboratory have addressed some the chemistry involved in the absorption of NO by ferrous cysteine (3,4). We have also recently communicated preliminary results concerning the use of ferrous chelates of certain cysteine derivatives in the removal of NO from the gas (5). This paper presents a full account of the scrubber chemistry of NO and  $\text{SO}_2$  removal by alkaline solutions containing ferrous chelates of the aforementioned SH-containing amino acids, as well as subsequent regeneration of the thioamino acids for recycling in the scrubber system.

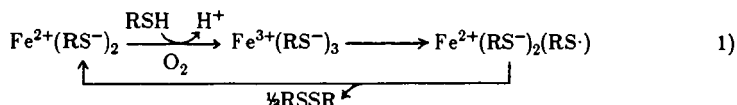
## EXPERIMENTAL

The absorption of NO by neutral or alkaline solutions of ferrous thioamino acid complexes was studied using a bench-scale gas scrubber and a Thermoelectron Model 14A chemiluminescent  $\text{NO}_x$  analyzer (3). For the reduction of the disulfide form of the

thioamino acids, a method similar to that developed for the regeneration of cysteine from cystine was used (4). The identification of all thioamino acids and their derivatives was performed on an amino acid analyzer built in-house (6). The determination of iron-, nitrogen-, and thioamino acid-containing products was based on analytical techniques described previously (3,4).

## RESULTS AND DISCUSSION

The removal of NO from oxygen-containing flue gas can be effected by aqueous solutions containing ferrous chelates of SH-containing amino acids, as shown in Figure 1. It is clear that all the ferrous thioamino acid complexes we tested are much more effective in absorbing NO than  $\text{Fe}^{2+}(\text{EDTA})$  under the same conditions. The greater NO absorption capacity in the cases of ferrous thioamino acid complexes may be accounted for by the ability of the thiol groups to reduce any ferric ion formed upon oxidation of the ferrous chelate by residual  $\text{O}_2$  in flue gas (Equation 1):



This mechanism is well established for  $\text{Fe}^{2+}(\text{Cys})_2$  (7) and is likely also applicable to  $\text{Fe}^{2+}(\text{AcCys})_2$ . In the case of Pen, it has been suggested that the two  $\beta$ -methyl groups serve to inhibit the oxidation-reduction reactions (8). It is therefore likely that the enhanced NO absorption capacity using  $\text{Fe}^{2+}(\text{Pen})_2$  and  $\text{Fe}^{2+}(\text{AcPen})_2$  is the result of the stability of ferrous chelates towards  $\text{O}_2$ . In any case, the concentration of ferrous thioamino acid complex in the absorber is maintained, and NO removal can therefore be sustained. On the contrary, the  $\text{Fe}^{3+}(\text{EDTA})$  complex formed upon oxidation is inactive towards NO. A further advantage of the ferrous thioamino acid systems is that the rapid intramolecular reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  can prevent the formation of dithionate ion resulting from the reaction between  $\text{Fe}^{3+}$  and  $\text{HSO}_3^-$ .

The effect of pH on the NO absorption capacity of ferrous thioamino acid complexes, as represented by the number of moles of NO absorbed per mole of  $\text{Fe}^{2+}$  used ( $n\text{NO}/n\text{Fe}^{2+}$ ), is shown in Figure 2. While the NO absorption capacity of  $\text{Fe}^{2+}(\text{Cys})_2$  is fairly insensitive to pH,  $\text{Fe}^{2+}(\text{Pen})_2$ ,  $\text{Fe}^{2+}(\text{AcCys})_2$ , and  $\text{Fe}^{2+}(\text{AcPen})_2$  are more efficient as the solutions become less basic, up to  $\text{pH} \sim 6$ . The influence of pH on NO absorption can be attributed to the presence of various ionic forms of thioamino acid, the stability constants of ferrous thioamino acid complexes and ferrous hydroxide, and the rate of  $\text{Fe}^{2+}$ -catalyzed oxidation of the thioamino acids by  $\text{O}_2$ .

The effects of several additives on the NO removal efficiency of  $\text{Fe}(\text{Cys})_2$  were examined, and the results are summarized in Table I (below). Power plant flue gas typically contains several thousand ppm  $\text{SO}_2$ , which dissolves in scrubbing liquors to form primarily  $\text{SO}_3^{2-}$  at  $\text{pH} > 9$ . The effect of  $\text{SO}_2$  on the NO absorption capacity can therefore be studied by the addition of  $\text{SO}_3^{2-}$  to the ferrous cysteine solution. Our results show that  $\text{SO}_3^{2-}$  can improve the NO removal efficiency of  $\text{Fe}^{2+}(\text{Cys})_2$ . Such enhancement could be a result of the reaction of  $\text{SO}_3^{2-}$  with  $\text{O}_2$  to form  $\text{SO}_4^{2-}$ , and/or the reaction of  $\text{SO}_3^{2-}$  with the oxidized product cystine ( $\text{CySSCy}$ ) to form  $\text{CySH}$  and cysteine sulfonate ( $\text{CySSO}_3^-$ ), *vide infra*. High concentrations of  $\text{S}_2\text{O}_3^{2-}$  can also enhance the NO removal efficiency of  $\text{Fe}^{2+}(\text{Cys})_2$ , probably because  $\text{S}_2\text{O}_3^{2-}$  can serve as an oxidation inhibitor. It is expected

Table I. Effects of Various Additives on NO Absorption Capacity of Ferrous Cysteine <sup>a</sup>		
Additive	Concentration, M	nNO/nFe <sup>2+</sup>
none	—	0.023
Na <sub>2</sub> SO <sub>3</sub>	0.05	0.040
	0.10	0.050
	0.50	0.068
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	0.05	0.030
	1.00	0.080

<sup>a</sup> The concentrations of Fe<sup>2+</sup> and CySH were 0.01 M and 0.04 M, respectively. The reaction was carried out at pH 9.5 (borate buffer) and 55 °C using a gas mixture of 500 ppm NO, 4% O<sub>2</sub> and the balance N<sub>2</sub>.

that SO<sub>3</sub><sup>2-</sup> and S<sub>2</sub>O<sub>3</sub><sup>2-</sup> will also improve the NO removal efficiency for other ferrous thioamino acid complexes. However, the extent of the improvement may not be as much as that in the Fe<sup>2+</sup>(CyS)<sub>2</sub>, since the adverse effect of O<sub>2</sub> is not as pronounced in those systems (5).

The reaction products collected from the NO absorption reactions by Fe<sup>2+</sup>(CyS)<sub>2</sub> and Fe<sup>2+</sup>(Pen)<sub>2</sub> were analyzed. It has been shown (3) that an iron dinitrosyl complex with an empirical formula [Fe(CySSCy)(NO)<sub>2</sub>] can be isolated when the reaction of NO and Fe<sup>2+</sup>(CyS)<sub>2</sub> was carried out in the absence of O<sub>2</sub>. The same dinitrosyl complex was not found in the presence of 4% O<sub>2</sub>, nor could an analogous iron nitrosyl complex be detected in the case of Fe<sup>2+</sup>(Pen)<sub>2</sub>, whether or not O<sub>2</sub> was present. In both the Fe<sup>2+</sup>(CyS)<sub>2</sub> and Fe<sup>2+</sup>(Pen)<sub>2</sub> systems, most of the absorbed NO was reduced to N<sub>2</sub> and N<sub>2</sub>O, and a small amount (<10% of the NO absorbed) of NO<sub>2</sub><sup>-</sup> was also detected in solution. As a result, minimal formation of of nitrogen-sulfur compounds is expected from the reaction between NO<sub>2</sub><sup>-</sup> and HSO<sub>3</sub><sup>-</sup> in the ferrous thioamino acid systems. On the other hand, > 90% of the iron was recovered as insoluble hydroxides in the solid residue, of which ~ 80% was Fe (II) and ~ 20% was Fe (III). The mass balance for the thioamino acid in the NO absorption reaction by Fe<sup>2+</sup>(CyS)<sub>2</sub> was also studied. In the absence of SO<sub>3</sub><sup>2-</sup>, all of the CySH were recovered as CySSCy, as shown in Figure 3. However, if SO<sub>3</sub><sup>2-</sup> as added to the Fe<sup>2+</sup>(CyS)<sub>2</sub> solution, CySSO<sub>3</sub><sup>-</sup> was also formed. It appears that the decrease in [CySSCy] and the increase in [CySSO<sub>3</sub><sup>-</sup>] are linear with respect to increasing [SO<sub>3</sub><sup>2-</sup>]. In each case, 96 ± 2% of the CySH can be recovered as a combination of CySSCy and CySSO<sub>3</sub><sup>-</sup>. It is clear from Figure 3 that unless high concentrations (> 0.5 M) of SO<sub>3</sub><sup>2-</sup> are present, most of the CySH would end up as CySSCy. It is therefore necessary to convert CySSCy back to CySH in order to make this process recyclable and cost-effective.

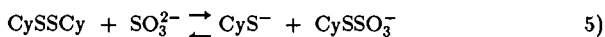
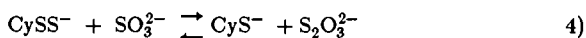
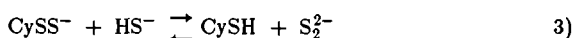
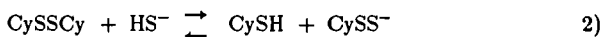
Existing methods for converting CySSCy to CySH require the use of electric energy or expensive reagents, which are not suitable for large-scale applications in flue gas clean up systems. We have discovered a simple and potentially cost-effective method for the regeneration of CySH from CySSCy using H<sub>2</sub>S (or sulfide/hydrogen sulfide ion) and SO<sub>2</sub> (or sulfite/bisulfite) (4). The results for the regeneration of CySH from CySSCy are presented in Table II (below). Methods I (sequential) and II (simultaneous) involve the treatment of a 40 mM CySSCy solution with two equivalents of Na<sub>2</sub>S·9H<sub>2</sub>O and three equivalents of Na<sub>2</sub>SO<sub>3</sub>. Similarly, H<sub>2</sub>S and SO<sub>2</sub> were used to treat the same CySSCy solution, sequentially in Method III and simultaneously in Method IV. The best result was obtained from the reaction of CySSCy with H<sub>2</sub>S and then SO<sub>2</sub> at pH 10 and 60 °C (Method III). The concentrations of HS<sup>-</sup> and SO<sub>3</sub><sup>2-</sup> in solution were estimated to be 0.04

**Table II. Regeneration of CySH from CySSCy under Various Conditions**

Method <sup>a</sup>	pH	T°, °C	CySH, %	CySSO <sub>3</sub> <sup>-</sup> , %	CySSCy, %
I	10	60	59	17	15
II	10	60	36	3	58
III	10	60	90	5	4
IVa	10	60	85	8	6
IVb	10	80	84	10	6
IVc	12	60	84	6	5

<sup>a</sup>See text for description of experimental methods.

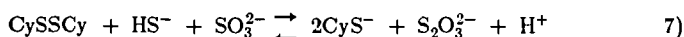
M and 0.22 M, respectively. In this case, a 90% yield of CySH was attained, which increased to 95% upon neutralization of the reaction mixture to pH ~ 7. The concentration-time profile of this reaction is shown in Figure 4. The mechanism for the conversion of CySSCy to CySH can be summarized by the following equations:



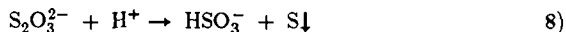
where  $\text{CySS}^-$  represents S-thiocysteine.

In the present study, we have determined that the disulfides of AcCySH and Pen were formed upon the reaction of respective thioamino acid and  $\text{Fe}^{3+}$ . The same  $\text{H}_2\text{S}/\text{SO}_2/\text{OH}^-$  treatment for the regeneration of CySH from CySSCy can be successfully applied to the regeneration of AcCySH from its disulfide. However, the reduction of Pen disulfide did not occur under the same conditions even after 48 hours. As mentioned above, this could be due to the steric effects of the two  $\beta$ -methyl groups in Pen. Therefore, development of a new method to regenerate Pen, and possibly AcPen, from the scrubbing liquor is needed.

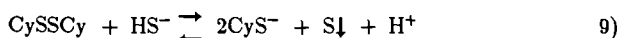
The overall reaction for the regeneration of CySH from CySSCy using  $\text{HS}^-$  and  $\text{SO}_3^{2-}$  can be expressed as



In an acidic medium,  $\text{S}_2\text{O}_3^{2-}$  decomposes to form  $\text{HSO}_3^-$  (and/or  $\text{SO}_2$ ) and colloidal sulfur, as shown in Equation 8.



By adding equations 7 and 8 and taking into account the equilibrium between  $\text{SO}_3^{2-}$  and  $\text{HSO}_3^-$ , we obtain the net equation



Thus, the only reagent consumed in the conversion of CySSCy to CySH is  $\text{HS}^-$ , and elemental sulfur is formed as a product. The latter can be converted back to  $\text{H}_2\text{S}$  by reaction with  $\text{H}_2$ , which can be derived from CO and  $\text{H}_2\text{O}$  (9). Therefore, in essence, the reducing agent consumed in this CySH and the corresponding AcCySH regeneration scheme is CO, which can be easily obtained from the incomplete combustion of coal. It can be inferred from Equation 9 that one mole of CO is required for the regeneration of two moles of CySH or AcCySH.

## CONCLUSIONS

Wet flue gas clean-up systems based on ferrous chelates of thioamino acids possess several major advantages over the conventional  $\text{Fe}^{2+}$  (EDTA) type chelates. These include higher NO absorption capacities, the suppression of dithionate and N-S compound formations, and the ability of the thioamino acids to reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  ion, thus eliminating the need to regenerate ferric chelates from the scrubbing liquor. Reduction of the oxidation products cystine and N-acetylcystine can be accomplished by treatment with  $\text{H}_2\text{S}$  and  $\text{SO}_2$  in basic solutions. However, the same process is not applicable to penicillamine, and possibly N-acetylpenicillamine, due to steric effects. Unfortunately, the application of these ferrous thioamino acid chelates in spray drying systems is limited by the larger stoichiometric ratio of the ferrous chelates to NO (Figure 2) required for obtaining a high ( $\geq 50\%$ ) NO removal efficiency.

## ACKNOWLEDGEMENT

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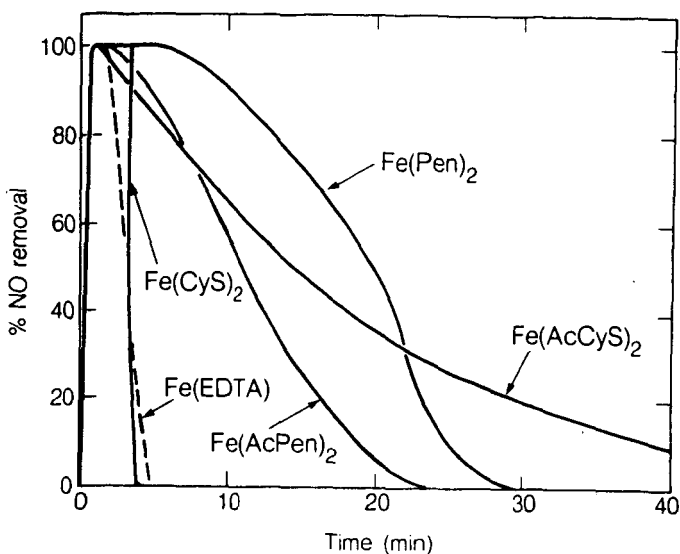


Figure 1. The NO removal efficiency of ferrous thioamino acid and  $\text{Fe}^{2+}$  (EDTA) chelates. Reaction conditions were:  $[\text{Fe}^{2+}] = 0.01 \text{ M}$ ; [thioamino acid] = [EDTA] =  $0.04 \text{ M}$ ;  $[\text{B}_4\text{O}_7^{2-}] = 1.18 \text{ M}$ ;  $P_{\text{NO}} = 500 \text{ ppm}$ ;  $P_{\text{O}_2} = 4\%$ ; pH = 7.0;  $T = 55^\circ\text{C}$ .

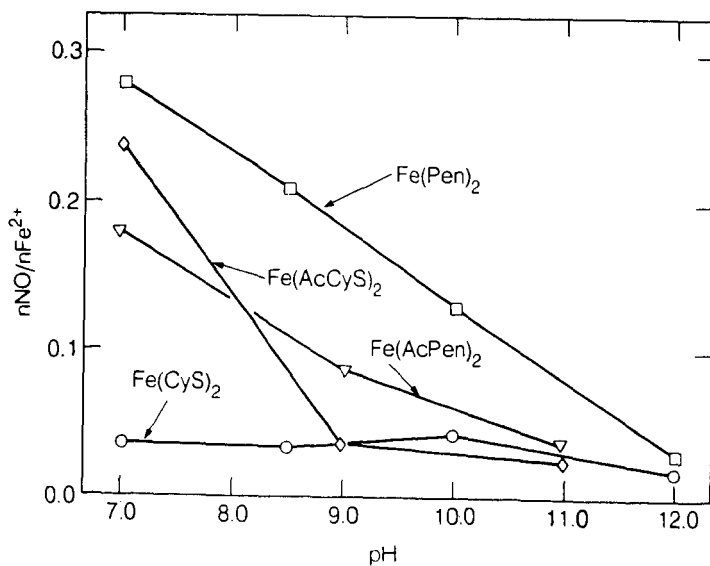


Figure 2. The NO absorption capacity of ferrous thioamino acid chelates as a function of pH. Reaction conditions were:  $[\text{Fe}^{2+}] = 0.01 \text{ M}$ ;  $[\text{CySH}] = 0.04 \text{ M}$ ;  $[\text{B}_4\text{O}_7^{2-}] = 0.09 \text{ M}$ ;  $P_{\text{NO}} = 500 \text{ ppm}$ ;  $T = 55^\circ\text{C}$ .

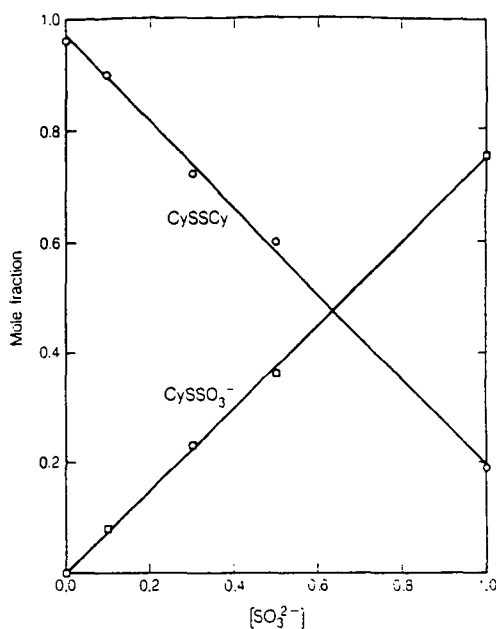


Figure 3. Recovery of CySH as CySSCy and  $\text{CySSO}_3^-$  at various  $[\text{SO}_3^{2-}]$ . Reaction conditions were:  $[\text{Fe}^{2+}] = 0.1 \text{ M}$ ,  $[\text{CySH}] = 1.0 \text{ M}$ ;  $[\text{B}_4\text{O}_7^{2-}] = 0.2 \text{ M}$ ;  $P_{\text{NO}} = 500 \text{ ppm}$ ;  $P_{\text{O}_2} = 4\%$ ;  $\text{pH} = 9.0$ ;  $T = 55^\circ \text{C}$ .

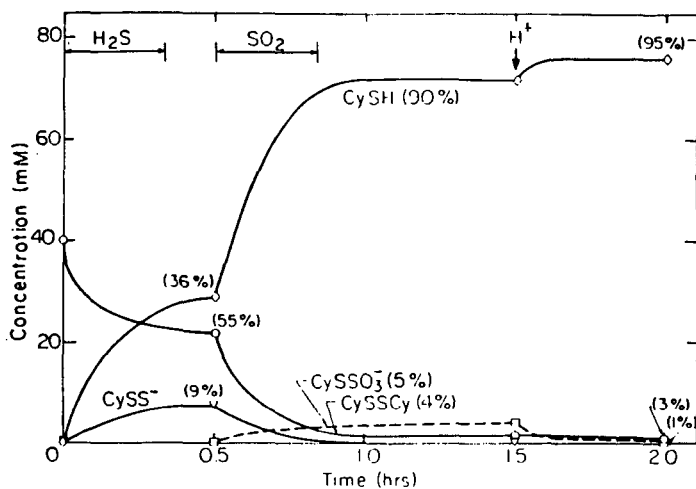


Figure 4. The concentration-time profile of the regeneration of CySH from CySSCy at pH 10 and  $60^\circ \text{C}$  by the reaction of CySSCy first with  $\text{H}_2\text{S}$  and then  $\text{SO}_2$ , followed by neutralization to  $\text{pH} \sim 7$ .